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PROPERTIES, STRUCTURE, AND APPLICATION OF LOW-MELTING LEAD–BISMUTH GLASSES

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Glass formation, crystallization, and physicochemical properties, as well as glass structure in the system $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, are investigated in the section with a constant molar content of glass-formers ($\text{B}_2\text{O}_3 + \text{SiO}_2$) equal to 20%. A nonlinear dependence of glass properties on their composition is established caused by the change of the coordination state of lead ion in glass structure. The developed glasses are recommended for joint and seals in the production of a new generation of physical parameter sensors.

The great interest in low-melting solder glasses is primarily due to the possibility of obtaining vacuum-dense joints under relatively low temperatures. A low soldering temperature prevents oxidation and deformation of metallic parts in the soldering zone, which might be damaged at higher temperatures. Joints based on low-melting glasses are homogeneous and in the case of an appropriate selection of TCLEs are free from stresses. Low-melting solder glasses are successfully used in vacuum technology and electronics as solders and protective and sealing coatings for semiconductor devices and integral circuits. They have obvious advantages in water-tightness and strength over organic dielectrics used for hermetic sealing and insulation of semiconductors.

A convenient basis for synthesis of low-melting solder glasses is a lead–bismuth glass-forming system, since lead and bismuth oxides provide for a low melting point.

The purpose of the present study is the development of new low-melting solder glasses in the multicomponent system $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ and studying their properties and structure. The choice of the system to be investigated is primarily due to the fact that it contains low-melting components PbO , ZnO , Bi_2O_3 , and B_2O_3 , which due to their high polarizability of cations ensure a low melting temperature in glass. Furthermore, bismuth oxides is a good adhesion activator.

Glass formation, physicochemical properties, and structure of glasses of the $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ systems have been studied in a section with a constant content of glass-forming components ($\text{B}_2\text{O}_3 + \text{SiO}_2$) equal to 20% (here and elsewhere molar content indicated). As a result, a range of glass-forming compositions was identified, which is limited by the following contents of the components (%): 5–50 PbO , 10–30 ZnO , 10–65 Bi_2O_3 . The glass forma-

tion diagram is shown in Fig. 1. Synthesis at 1000°C yielded clear glasses that did not crystallize in their production. Compositions outside the specified oxide concentration bounds crystallized in casting.

The relatively low content of traditional glass-formers, i.e., boric anhydride and silicon oxide (20%), is evidence of the capacity of other system components, namely lead and bismuth, for glass formation. Some authors [1–4] note the

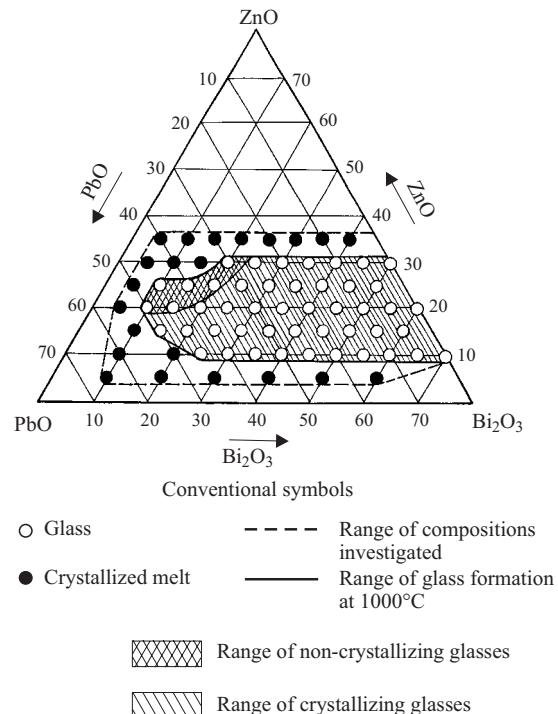


Fig. 1. Diagram of glass formation and crystallization of glasses in system $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$.

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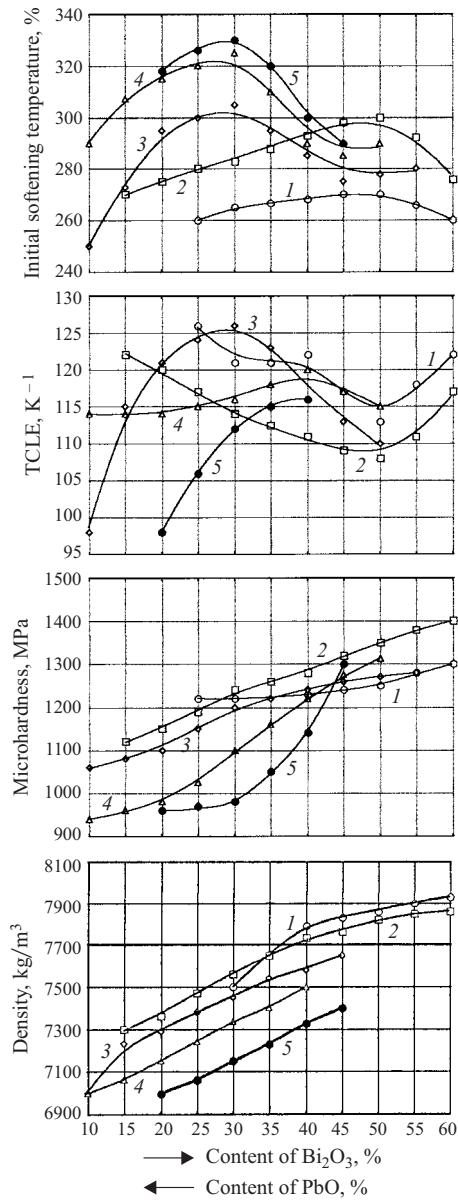


Fig. 2. Dependence of physicochemical properties of glasses on their composition with ZnO content equal to 10 (1), 15 (2), 20 (3), 25 (4), and 30% (5) and equimolar replacement of PbO by Bi_2O_3 .

dual role of lead ions in glass structure: that of a modifier and a glass-former of the glass structural lattice. The Pb^{2+} ion in lead-borate, lead-silicate, and lead-borosilicate glasses with a low content of PbO acts as a modifier in the form of $[\text{PbO}_6]$ groups. At a high concentration, its effect as a glass-forming agent is manifested in the form of tetrahedra $[\text{PbO}_4]$. It was earlier noted [2–4] that the concentration threshold above which the lead ion behaves as a glass-former varies from 20 to 50% PbO.

Bismuth ions, similarly to lead ions, can be incorporated in the structural lattice of glass. This is corroborated by the similarity of their atomic weight, ionic radius, and electron configuration of their atoms [5]. Analyzing data on glass for-

mation in binary bismuth-bearing borate and silicate systems [6–8] and comparing them to the results of our studies, one can assume the glass-forming capacity of bismuth oxide and its structural role as a glass-forming agent. The results of our studies do not contradict published data but support and complement them. The glass-formation boundary in the system considered with the maximum content of 50% PbO and 65% Bi_2O_3 demonstrates that both oxides act as glass-formers in the structure of experimental glasses.

The study of the crystallization properties of glasses in the system $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ established their high crystallizing capacity. The results of mass gradient crystallization revealed the existence of a narrow composition range of clear glasses that do not crystallize under heat treatment. Glasses with a stable vitreous state contain (%) 10–20 Bi_2O_3 , 30–50 PbO, and 20–30 ZnO (see Fig. 1). An ample range is taken by glasses crystallizing under heat treatment, which are interesting for developing low-melting glass cements.

In studying the crystallizing capacity of glasses using differential thermal analysis, the effect of the chemical composition of glasses on their crystallizing capacity was established. Thermograms of glasses with a constant content of ZnO under equimolar replacement of PbO by Bi_2O_3 in a temperature range of 450–510°C exhibit exothermic effects caused by formation of crystalline phases. X-ray phase analysis of the products of crystallization of glasses heat-treated within this temperature interval identified the formation of bismuth borate $12\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ as the main crystalline phase and, possibly, bismuth silicate $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$, since their interplanar distances coincide (0.318, 0.290, 0.269, 0.238, and 0.173 nm). Furthermore, compositions with a high content of lead oxide (30–40%) exhibit the formation of lead–bismuth borates $6\text{PbO} \cdot \text{Bi}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$.

Bismuth oxide has a substantial effect on the process of glass crystallization. As the concentration of Bi_2O_3 increases, the shape and the level of the exothermic curve change. Wide peaks of low height transform into a narrower and better defined contour, become elongated, and shift toward the low-temperature range, which indicates increased crystallization capacity of glasses. The reason for the high crystallization capacity of glasses is their microheterogeneous structure. Electron-microscope analysis of glasses corroborated the existence of heterogeneous zones of the liquation type.

As a result of studying the physicochemical properties of experimental glasses, the nonlinear dependence of the initial softening temperature, the TCLE, and microhardness of glass on its composition was established (Fig. 2). The composition–property curves have an inflection in the range of PbO content around 20% caused by structural rearrangements in glasses. Under equimolar replacement of PbO by Bi_2O_3 , with ZnO content growing from 10 to 30%, the extremum is shifted toward a higher content of bismuth oxide (from 30 to 50%) and correlates with 20% PbO for all glass compositions. It can be inferred that coordination restructur-

ing of lead ions occurs within the range of approximately 20% PbO, and the structural role of lead in glass changes. Apparently, up to 20% PbO the lead ion acts as a modifier of the structural glass lattice and when its content is higher, its glass-forming effect is manifested. It is established that the initial softening temperature of experimental glasses lies within the limits of 250 – 330°C. The TCLE of glasses varies in a wide range from 98×10^{-7} to $126 \times 10^{-7} \text{ K}^{-1}$. As the PbO content grows to 20%, the initial softening temperature increases, and the TCLE decreases, which is easily explicable: Pb²⁺ ions being structural modifiers, occupy in the voids of the structural glass lattice, condense it, and contribute to raising the initial softening temperature of glasses and decreasing their TCLE. In glasses containing 20 – 30% ZnO the course of these curves is different, namely, as the content of PbO grows to 20%, the initial softening temperature and the TCLE of glasses increase. Such mutual dependence of the properties specified was observed by us in zinc-containing lead-tellurite glasses [4]. The same dependence was earlier registered for zinc-containing lead-borate glasses [5].

The microhardness of glasses considered is equal to 940 – 1400 MPa depending on their compositions. The low microhardness values are due to the fact that glass compositions contain cations with a large ionic radius: Pb²⁺ (1.26 Å) and Bi³⁺ (1.20 Å), which decrease microhardness. With equimolar replacement of PbO by Bi₂O₃ microhardness grows.

The experimental glasses have high density: 7000 – 7920 kg/m³. The presence of heavy metal oxides in glasses to some extent contributes to glass density values. Since the atomic weight of bismuth is higher than the atomic weight of lead, equimolar replacement of PbO by Bi₂O₃ leads to increased density.

The structure of the glasses was investigated by IR spectroscopy. It should be noted that the structure of multi-component glasses containing oxides of heavy metals, i.e., lead and bismuth, is little studied and data on the coordination state of their ions in glass structure are scarce. It is known [9] that bismuth ions, due to their high polarizability, can form deformed asymmetric octahedra [BiO₆], which create a spatial structural lattice and constitute the main structural pattern in these glasses. Bismuth ions in glass may exist in six- and eight-coordination [10]. It was mentioned above that lead ions can fulfill a dual role in glass structure depending on the PbO concentration. However, none of published sources present absorption bands typical of lead and bismuth ogegen groups. The existence of lead and bismuth ions in a certain coordination may be indirectly inferred from their effect on the main structural groups in glass.

An IR-spectroscopic study of a series of glasses with a constant content of ZnO (10, 15, 20, 25, and 30%) with equimolar replacement of PbO by Bi₂O₃ was performed. Since all the absorption spectra of the glasses considered are identical, Fig. 3 shows absorption spectra of a series of glasses with a constant content of ZnO. The absorption spec-

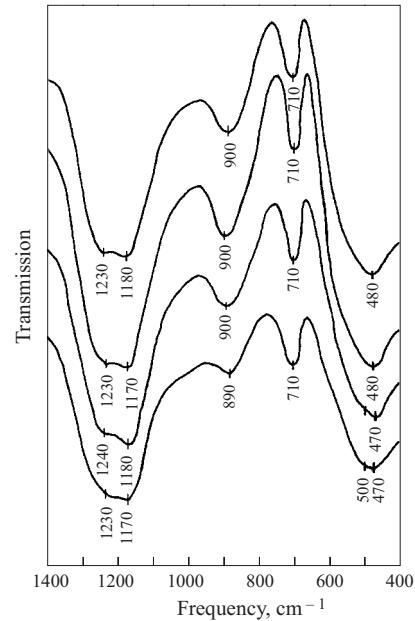


Fig. 3. IR absorption spectra of glasses under equimolar replacement of PbO by Bi₂O₃ and a constant content of ZnO (10%).

tra are characterized by four groups of absorption bands: an intense wide band with two maxima in the range of 1180 – 1250 cm⁻¹ and absorption bands at 900, 710 – 720, and 480 cm⁻¹. The absorption bands at 1180 – 1250 and 710 – 720 cm⁻¹ correspond to trigonally coordinated boron in boroxol rings and chain links of triangles [BO₃]. The presence of a maximum at 1180 cm⁻¹ suggests that [BO₃] groups in the glass structure are linked in chain structures. The maximum at 1250 cm⁻¹ and the band at 710 cm⁻¹ are evidence of the presence of [BO₃] groups, either isolated or joined in boroxol rings in the glass structure. The absorption band with the maximum at 900 cm⁻¹ may be due to the presence of isolated silicon-oxygen tetrahedra [SiO₄].

Interpretation of absorption bands in the low-frequency spectrum range at 480 cm⁻¹ is difficult to make due to superposition of characteristic absorption bands of different structural groups. In this spectrum range one can expect the emergence of absorption bands corresponding to deformation vibrations of groups ν_s SiO₄ and ν_s ZnO₄ [10].

Analysis of spectra indicated that equimolar replacement of PbO by Bi₂O₃ with a constant content of ZnO, as well as an increasing concentration of ZnO, do not change the form of the spectrum. Consequently, a change in the content of lead and bismuth in glass and their equimolar replacement do not affect the structural groups of boron. Lead and bismuth oxides presumably form their own spatial lattice causing phase separation in glasses. This accounts for the high crystallization capacity of experimental glasses. Based on experimental data, it can be assumed that the glass structure is represented by the borate component, in which single silicon-oxygen tetrahedra are located, and the lead–bismuth component.

Thus, as a consequence of studies performed, glass formation bounds in the $\text{PbO} - \text{ZnO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system and ranges of clear glasses and glasses crystallizing under heat treatment were identified and localized on the phase diagram.

Lead-bismuth glasses have been developed and optimized, which have the following parameters: temperature of synthesis $950 \pm 50^\circ\text{C}$, initial softening temperature $250 - 330^\circ\text{C}$, TCLE $(98 - 126) \times 10^{-7} \text{ K}^{-1}$, microhardness $940 - 1400 \text{ MPa}$, density $7000 - 7920 \text{ kg/m}^3$, soldering temperature not higher than 500°C .

New compositions of low-melting lead-bismuth glasses are recommended as solder and sealing materials for advanced technologies in the production of sensitive quartz elements for temperature and pressure sensors and accelerometers of high precision. Lead-bismuth glasses obtained are promising for designing and producing new types of measuring instruments: new-generation quartz sensors.

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